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(54) Fluoroelastomers with improved processability and process for preparing them.

(57) Described are fluoroelastomers characterized by the presence of iodine and/or bromine atoms at the end of the polymeric chain, in an amount of at the most one iodine and/or bromine atom per polymeric chain, and by a bromine content within the chain ranging from 0.05 to 2% by weight, based on the total weight of the monomeric units.

Said fluoroelastomers exhibit improved processability, particularly as regards their use in injection moulding and the release from the moulds, as well as an improved heat stability.

A process for preparing said fluoroelastomers is also disclosed.

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FLUROELASTOMERS WITH IMPROVED PROCESSABILITY AND PROCESS FOR PREPARING THEM

The present invention relates to new elastomeric fluorinated polymers endowed with improved processability as well as to a process for preparing them.

As it is known, elastomeric fluorinated copolymers, in particular those based on vinylidene fluoride (VDF), hexafluoropropene (HFP) and on other monomers such as tetrafluoroethylene (TFE) and fluorinated vinyl ethers (FVE), have a broad field of application, owing to their properties in the vulcanized state such as stability to heat, to atmospheric and chemical agents in general, and to sunlight. Said polymers are predominantly prepared by copolymerization of the above fluorinated monomers, in suitable ratios, in the presence of radical starters of the peroxide type, activated thermally or by means of redox systems.

A requirement of the industry which prepares and uses fluoroelastomeric polymers is that said products should be promptly and economically vulcanizable. In particular required are: high vulcanization rates, a significant increase in the torque value during the ODR vulcanization test, easy release of the vulcanized products from the moulds, low compression set values of the vulcanizates and, finally, sufficiently low viscosity values of the vulcanization mixtures to permit an easy use of said mixtures, mainly in injection moulding.

Several attempts have been made to obtain fluoroelastomers which are satisfactory in said respects. US-A-4 035 565 describes fluorinated copolymers which comprise up to 3% by moles of units derived from bromotrifluoroethylene or 4-bromo-3,3,4,4-tetrafluorobutene-1 and are based on monomeric units derived from combinations of tetrafluoroethylene and C₂-C₄ olefins and, optionally, vinylidene fluoride, or from combinations of tetrafluoroethylene and perfluoroalkyl-perfluorovinylethers, or of perfluoroalkyl-perfluorovinylethers and fluorinated olefins.

Said copolymers exhibit excellent thermal stability but can be processed only with difficulty, due to the adhesion and to the residues that they leave on the surfaces of the vulcanization moulds.

FR-A-2 386 561 discloses readily vulcanizable fluorinated copolymers, consisting of monomeric units derived from vinylidene fluoride and, optionally, of one or more fluoroolefins, comprising at least one iodine atom per polymeric chain, said iodine atom being situated at the end of the chain and being derived from iodinated chain transfer agents (RI)_x and, furthermore, comprising within the polymeric chain, fluorohydrocarbon residues R derived from the above chain transfer agents.

Said copolymers are prepared by (co)polymerization of suitable fluorinated monomers, in the presence of the above iodinated transfer agents and a source of free radicals, such as light irradiation, peroxides, etc.

The products thus obtained are promptly vulcanizable and do not exhibit adhesion to the moulds during vulcanization. They show, however, a low thermal stability.

Thus, one of the objects of the present invention is to provide readily vulcanizable elastomeric fluorinated copolymers, endowed with improved processability (especially in injection moulding), which do not cause adhesion to the moulds during moulding processes, both in a press and by injection, and which, at the same time, possess a satisfactory thermal stability.

The fluoroelastomeric copolymers according to the present invention comprise monomeric units derived from vinylidene fluoride and/or tetrafluoroethylene, said units being optionally combined with monomeric units derived from hexafluoropropene and/or perfluoroalkyl-perfluorovinylethers, and are characterized in that they contain, in an end position of the polymeric chain, a halogen atom selected from iodine and bromine or mixtures thereof, in an amount equal to or less than one halogen atom per polymeric chain, and are further characterized by a content of non-terminal bromine atoms, deriving from brominated monomeric units in the polymeric chain, ranging from 0.05 to 2% by weight, based on the total weight of the monomeric units present in the chain.

Monomeric units derived from ethylene and/or propylene and/or butene-1 and/or isobutene, can be present in such copolymers in amounts up to 40% by moles, based on the total moles of the fluorinated monomeric units.

The content of bromine and/or iodine located at the ends of the polymeric chains generally ranges from 0.001 to 1% by weight, but preferably from 0.04 to 0.6% by weight, based on the total weight of the monomeric units which are present in the polymer.

Preferably, iodine is the halogen which is present in the end positions of the polymeric chains.

Examples of brominated monomeric units present in the copolymers that can be mentioned are those which are derived from polymerizable brominated compounds such as the compounds of general formula Br-CF₂-Rf-O-CF=CF₂, where Rf is a perfluorinated alkylene group containing from 1 to 9 carbon atoms, or derived from brominated olefins such as bromotrifluoroethylene, 4-bromo-3,3,4,4-tetrafluorobutene-1 and, in general, olefins wherein at least one hydrogen atom has been substituted by a bromine atom and,

optionally, one or more of the remaining hydrogen atoms have been substituted by another halogen atom, preferably fluorine. Some olefins of this type are preparable according to methods known in the art, for example, as described by Tarrant and Tunden in J. Org. Chem. 34, 864 (1969) and by Fainberg and Miller in JACS 79, 4170 (1957). Other brominated olefins which may be copolymerized and, thus, can form
 5 brominated monomeric units contained in the products of the present invention are vinyl bromide, 1-bromo-2,2-difluoroethylene, perfluoroallylbromide, 4-bromo-1,1,2-trifluorobutene, 4-bromo-1,1,3,3,4,4-hexafluorobutene, 4-bromo-3-chloro-1,1,3,4,4-pentafluorobutene, 6-bromo-5,5,6,6-tetrafluorohexene, 4-bromo-perfluorobutene-1 and 3,3-difluoroallylbromide.

Among the monomeric perfluoroalkyl-perfluorovinylether bits the preferred ones are those which are
 10 derived from compounds of general formula $CF_2=CF-O-R_f$, wherein R_f is a perfluoroalkyl radical containing from 1 to 5 carbon atoms and, preferably, from 1 to 3 carbon atoms (for example, CF_3 or C_2F_5).

The fluoroelastomeric copolymers of the present invention result - the qualitative and quantitative composition being identical - in vulcanization mixtures endowed with improved processability in the molten state as compared with the corresponding bromine-modified copolymers of US-A-4 035 565, exhibit a
 15 detachability from the vulcanization moulds which is at least equal to that of the polymers modified with terminal iodine as described in FR-A-2 386 561, and, at the same time, possess a higher thermal stability than that of the products of said FR-A.

Furthermore, the fluoroelastomeric compounds according to the present invention are substantially free of gels (gel content lower than 1% by weight).

20 Additionally, said copolymers generally exhibit modulus values, after vulcanization under standard conditions and with identical vulcanization formulation, which are higher than those of the only chain-brominated copolymers or of the only iodinated copolymers with more than one terminal iodine atom.

Another object of the present invention is to provide a process for preparing elastomeric fluorinated copolymers containing, in the end position of the polymeric chain, iodine and/or bromine atoms in an
 25 amount equal to or less than one atom of said halogen per polymeric chain, which process comprises polymerizing, preferably in an aqueous emulsion, monomers selected from vinylidene fluoride, tetrafluoroethylene, hexafluoropropene, perfluoroalkyl-perfluorovinylethers and mixtures thereof in combination with at least one brominated polymerizable monomer by means of radical starters and in the presence of one or more compounds capable of providing, under the polymerization conditions, I^- or Br^- ions in the
 30 polymerization medium. Examples of compounds showing such characteristics and, therefore, utilizable in the process of the present invention are, in particular, hydroiodic (HI) and hydrobromic (HBr) acids, iodides and bromides of metals belonging to groups I and II, A and B, of the Periodic System such as, for example, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Cu, Ag, Zn and Cd, as well as of the transition metals such as, for example, Fe, Co, Ni, Ru, Rh, Pd and Pt, or belonging to groups III and IV B of the Periodic System such as,
 35 for example, Al, Ga, Sn and Pb.

Preferably, the iodides of the alkali or alkaline-earth metals are used. The molar amount of compounds capable of providing I^- and/or Br^- ions, to be used in the process of the invention is, preferably, higher than the molar amount of iodine and/or bromine combined in the end positions of the chains of the final polymer.

40 In practice, the amount of such compounds is usually higher by 30% by weight than the amount corresponding to the amount of terminal iodine and/or bromine present in the final polymer.

In addition to the above fluorinated monomers and polymerizable brominated monomers, olefinic monomers, in particular ethylene and/or propylene and/or butene-1 and/or isobutene, can be present in the polymerization mixture.

45 The above olefinic monomers can be employed in amounts up to 40% by moles with respect to the total moles of fluorinated monomers present in the polymerization mixture.

The process according to the present invention permits the preparation of fluoroelastomers containing, in the end positions of the polymeric chains, iodine and/or bromine atoms in an (average) amount not exceeding one atom per polymeric chain and, preferably, in an amount ranging from 0.1 to 0.9 atoms per
 50 polymeric chain.

In said fluoroelastomers the remaining ends of the polymeric chains can exhibit an end group stemming from the decomposition of the polymerization starter or from a possible reaction thereof with the polymerization medium. For example, when a persulphate is utilized as a polymerization starter, said end groups may be -OH or -COOH groups.

55 Alternatively, the other end groups can be derived from a suitable and known chain transfer agent introduced into the reaction medium in order to regulate the molecular weight of the polymer such as, for example, ethyl acetate, chloroform, etc.

The copolymerization reaction can be carried out by means of known methods such as, for example,

those described in Kirk Othmer, Encyclopaedia of Chemical Technology, Vol. 8, pages 500 and following, 1979. Said polymerization methods comprise bulk polymerization or polymerization in solution of organic solvents, or in emulsion or suspension in water. Useful radical polymerization starters are, for example, inorganic peroxides such as ammonium or potassium persulphates, redox systems such as persulphate-bisulphite and ferropersulphate, organic peroxides such as benzoyl peroxide, dicumyl peroxide, bis (4-t-butyl-cyclohexyl) peroxodicarbonate, di-t-butyl-peroxide, diisopropylperoxodicarbonate; diethylhexylperoxodicarbonate, acetyl-cyclohexyl-sulphonyl peroxide, t-butyl-peroxopivalate, 2,4-dichloro-benzoyl peroxide, isobutyl peroxide, octanoyl peroxide, fluorinated peroxides and peranhydrides.

Preferably, the polymerization is conducted in aqueous emulsion. Any type of (fluorinated) emulsifier can be used in the process of the present invention; examples thereof are the fluorinated carboxylic acid soaps.

The polymerization reaction can be conducted at temperatures ranging from 25° to 150°, under pressures up to 10 MPa.

Merely as examples of elastomeric fluorinated copolymers of the present invention may be mentioned those consisting of a combination of the following monomeric units, in the mole percentage indicated below:

20	I)	Vinylidene fluoride (VDF)	35-80
		Hexafluoropropene (HFP)	10-35
		Tetrafluoroethylene (TFE)	0-30
		Perfluoroalkylvinylether (FVE) (where the alkyl group can have 1 to 3 carbon atoms)	0-25
	II)	VDF	35-80
		FVE	10-35
		TFE	0-30
25	III)	TFE	53-80
		FVE	20-47
	IV)	TFE	30-65
		Hydrogenated (i.e., non-fluorinated) olefin containing from 2 to 4 carbon atoms	20-55
		VDF	0-40

The following examples serve to illustrate the invention without limiting the scope thereof.

35 EXAMPLES

Polymerization method and characterization of the copolymers

40 Use was made of an evacuated 5-liter reactor equipped with stirrer. The reactor was charged with 3,500 g of H₂O, optionally an ionic surfactant (such as ammonium perfluorooctanoate), and acidity buffer consisting of potassium metabisulphite in an amount such as to always maintain the pH value in the range of from 2 to 6 and, finally, all or part of the predetermined amount of the compound(s) capable of providing I⁻ and/or Br⁻ ions.

45 Pressure was generated in the reactor by introducing the monomer mixture then, after having brought the reactor temperature to the polymerization temperature, the radical starter, an aqueous solution of (NH₄)-₂S₂O₈ (150 g of persulphate/liter of H₂O), was added.

During the polymerization, starter and/or iodine and/or bromine ion generator compound were optionally added and the pressure was maintained constant by feeding the monomers in the indicated molar ratios.

50 Upon completion of the reaction, corresponding to the desired conversion, the emulsion was discharged and coagulated by means of conventional methods, for example, by addition of Al₂(SO₄)₃ or of acids. The polymer was separated, washed with water and dried in an air-circulation oven until the polymer showed a moisture content of less than 1%.

55 The polymer thus obtained was mixed in an open roller mixer with conventional vulcanization ingredients, in the weight percentages indicated below:

Polymer	100
Luperco ^(R) 101 XL	3
Triallylisocyanurate	4
PbO	3
Carbon black (MT Black)	30

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The mixture was subjected to the following measurements:

- 10 a) Mooney viscosity 1 + 10 at 121 °C (ASTM 1646/82).
 b) Mooney viscosity, scorch at 135 °C (ASTM 1646/82)
 c) ODR (oscillating disk rheometer) (ASTM D 2084/81) conducted at 180 °C, arc ± 3.

The mixture was then vulcanized in a press at 170 °C for 10 minutes, according to ASTM D 412/80.

The vulcanizate was subjected to the following measurements:

- 15 d) Measurement of the following mechanical properties:
 - Tensile modulus (M100)
 - Tensile strength (T.S.)
 - Elongation at break (E.B.)
 - Shore hardness A (Hard.);
- 20 e) Measurement of the above mechanical properties after post-treatment of the vulcanizate at 250 °C by raising up to 8 hours and permanent for 24 hours at 250 °C (ASTM D 412/80);
 f) Detachability from the mould according to the procedure indicated below:

The mixture was vulcanized in a press at 170 °C for 10 minutes and, thereafter, the test piece was removed from the mould at 170 °C.

- 25 The mould soiling was evaluated on a mould having 7 circular cavities (diameter = 40 mm, height = 3 mm) by repeating the moulding operations for all tested mixtures until differences on the bottom surfaces of the circular cavities (brown spots, i.e., darker opalescences) could be observed.

For each mixture, 80 moulding cycles were carried out. The evaluation scale was as follows:

- 30 10. No brown spots present after 80 moulding cycles.
 9. Brown spots present after 70 moulding cycles.
 8. Brown spots present after 62 moulding cycles.
 7. Brown spots present after 55 moulding cycles.
 6. Brown spots present after 49 moulding cycles.
 5. Brown spots present after 42 moulding cycles.
 35 4. Brown spots present after 35 moulding cycles.
 3. Brown spots present after 28 moulding cycles.
 2. Brown spots present after 21 moulding cycles.
 1. Brown spots present after 14 moulding cycles.
 0. Brown spots present after 7 moulding cycles.
- 40 g) Thermal stability on the vulcanized test pieces, post-treated at 275 °C for 70 hours (ASTM D 573/81 (E145)).
 h) Compression set at 200 °C for 70 hours after post-treatment at 250 °C by raising up to 8 hours and permanent for 24 hours (ASTM D 1414/78).

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Example 1

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Molar composition of the fed monomer mixture (percent):	
- HFP	25
- TFE	25
- VDF	50
Other reagents:	
- KI	4.2 g
- Starting $(\text{NH}_4)_2\text{S}_2\text{O}_8$	6.9 g

During polymerization, which lasted 129 minutes, the reactor was charged with 0.78 g of starter in intervals of 10 minutes and with KI in increments of 0.42 g after each 10% conversion of the monomers, as well as with $\text{CF}_2 = \text{CF}-\text{O}-\text{CF}_2-\text{CF}_2-\text{Br}$, in increments of 1.7 g after each 5% conversion of the monomers.

Polymerization temperature and pressure were 85°C and 1.7 MPa, respectively.

1500 g of a polymer having the following composition (determined by ^{19}F -NMR) were obtained (in mole percent):

- HFP	21.4
- VDF	53.8
- TFE	23.9

the balance to 100 consisting of brominated monomeric units, and containing 0.69% by weight of bromine (determined by fluorescence) based on the polymer weight. The polymer had an inherent viscosity of 0.42 dl/g.

This copolymer exhibited iodine atoms only in one of the end positions of the polymeric chains, in an amount of 0.47 atoms per polymeric chain, and corresponding to 0.14% by weight of iodine, based on the polymer. The copolymer was substantially gel-free. The above characteristics (a) to (h) of the vulcanization mixture and of the resulting vulcanizate are given in the table below.

Example 2 (Comparison)

The procedure of example 1 was repeated but without employing the brominated monomer and, furthermore, by using 5.4 g of KI. In the copolymer, the content of terminal iodine was 0.18% by weight, corresponding to 0.52 iodine atoms per polymeric chain. There was no gel content. The characteristics of the vulcanization mixture and of the corresponding vulcanizate are reported in the table below.

Example 3

Composition of the fluorinated monomers employed (in mole percent):	
- VDF	55
- Perfluoromethyl-vinylether (PMVE)	23
- TFE	22

The other polymerization conditions were similar to those of example 1, with the exception of the pressure, which was 1.9 MPa, and the total amount of KI, which was 3.6 g and was fed in 0.36 g increments after each 10% conversion of the monomer. The resulting polymer had the following composition (in mole percent):

- VDF	58.6
- PMVE	17.8
- TFE	23.6

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with a bromine content in the polymeric chain of 0.6% by weight and a terminal iodine content of 0.11% by weight, corresponding to 0.65 iodine atoms per polymeric chain. The gel content was 0%.

10 The characteristics of the vulcanization mixture and of the corresponding vulcanizate are reported in the table below.

Example 4

15 Example 3 was repeated, using the following fluorinated monomers (in mole percent):

- VDF	46
- HFP	5
- TFE	26
- PMVE	23

20

25 The resulting polymer had the following composition (in mole percent):

- VDF	48.4
- HFP	4.5
- TFE	27.4
- PMVE	19.1

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35 with a bromine content in the chain of 0.6% by weight and an iodine content in end position of 0.1% by weight, corresponding to 0.6 iodine atoms per polymeric chain. The inherent viscosity was 0.54 dl/g. The gel content was 0%. The characteristics of the mixture and the resulting vulcanizate are reported in the table below.

40 Example 5

Example 1 was repeated, with the exception that the pressure was 2.2 MPa and the amount of the starter was 2.8 g at the beginning and KI was added in 0.31 g portions per each 10% conversion of the monomers, using the following fluorinated monomers (in mole percent):

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- VDF	79
- HFP	21

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The polymer obtained exhibited the following composition (in mole percent):

- VDF	78.1
- HFP	21.7

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with a bromine content in the chain of 0.6% by weight, and a content of iodine in end position of 0.12% by

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weight, corresponding to 0.65 iodine atoms per chain. The inherent viscosity was 0.7 dl/g. The gel content was 0%. The characteristics of the vulcanization mixture and of the corresponding vulcanizate are reported in the table below.

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Table

Examples	Characteristics of the vulcanization mixtures and of the vulcanizates											
	a	b*	c				d					
			t min++ (lb. foot) inch	t max+++ (lb. foot) inch	Is ₂ (sec)	Is ₅₀ (sec)	T' 90	Vmax (lb. foot. inch) sec	M100 (MPa)	T.S. (MPa)	El. (%)	Hard.
1	16	12	4.5	77.5	60	129	252	1.11	5.5	14	220	71
2°	15	-	1.7	11.5	-	-	-	0.22	-	-	-	-
3	33	-	10	93	57	120	235	1.28	5.5	16.7	195	70
4	56	-	7.5	80	55	150	288	1.4	5	13.5	219	66
5	44	-	9	70	60	-	223	1.3	5.5	14.5	250	65

* minimum value after 15 minutes = 11' and 54"

++ minimum torque

+++ maximum torque

° no vulcanization occurs

Table (continued)

Examples	Characteristics of the vulcanization mixtures and of the vulcanizates									
	e				f	g		h		
	M100 (MPa)	T.S. (MPa)	Elong. (%)	Hard.		Δ M100 (%)	Δ T.S. (%)	Δ El. (%)	Δ Dm (%)	
1	7	19	200	73	10	- 52	- 47	+ 60	- 5	
2	-	-	-	-	-	-	-	-	-	
3	7	19	186	72	10	-70	- 55	80	- 7	
4	6.2	18.2	209	71	10	-70	- 78	70	- 4	
5	6	18	230	70	10	-21	- 45	5	- 1	

Claims

- 5 1. Elastomeric fluorinated copolymers comprising monomeric units derived from vinylidene fluoride and/or tetrafluoroethylene, optionally combined with monomeric units derived from hexafluoropropene and/or perfluoroalkyl-perfluorovinylethers, which contain terminal iodine and/or bromine atoms in an amount of, at the most, one iodine and/or bromine atom per polymeric chain and which contain bromine within the chain,
- 10 derived from brominated units of the polymeric chain, in an amount of from 0.05 to 2% by weight, based on the total weight of the monomeric units present in the polymer.
2. Copolymers according to claim 1, wherein the terminal iodine and/or bromine atoms of the polymeric chains represent from 0.001 to 1% by weight of the total weight of the monomeric units present therein.
3. Copolymers according to any one of claims 1 and 2, wherein the content of terminal iodine and/or
- 15 bromine atoms is from 0.04 to 0.6% by weight of the total weight of the monomeric units present therein.
4. Copolymers according to any one of claims 1 to 3, comprising up to 40% by moles, based on the total moles of fluorinated monomeric units, of units derived from an olefin selected from ethylene, propylene, butene, isobutene or mixtures thereof.
5. Process for preparing elastomeric fluorinated copolymers containing terminal iodine and/or bromine
- 20 atoms in an amount not exceeding one iodine and/or bromine atom per polymer chain, which process comprises polymerizing a monomer selected from vinylidene fluoride, tetrafluoroethylene, hexafluoropropene, perfluoroalkyl-perfluorovinylethers or mixtures thereof with at least one polymerizable brominated monomer by means of radical starters and in the presence of one or more compounds capable of providing, under the polymerization conditions, I^- and/or Br^- ions in the polymerization medium.
- 25 6. Process according to claim 5, which is carried out in aqueous emulsion.
7. Process according to any one of claims 5 and 6, wherein said brominated monomer is employed in an amount such as to provide a polymer containing from 0.05 to 2% by weight of bromine, based on the total weight of the monomer units.
8. Process according to any one of claims 5 to 7, wherein the mixture of monomers comprises up to 40%
- 30 by moles, based on the total moles of fluorinated monomers present therein, of an olefin selected from ethylene, propylene, butene-1, isobutene and mixtures thereof.
9. Process according to any one of claims 5 to 8, wherein the compounds capable of providing I^- or Br^- ions are iodides or bromides of alkali or alkaline-earth metals.
10. Process according to any one of claims 5 to 9, wherein alkali and/or alkaline-earth iodides are
- 35 employed.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 3078

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0055407 (ASAHI GLASS COMPANY LTD.) * examples 4-11; claims 1 and 4 *	1	C08F214/22 C08F214/26 C08F2/38
X	EP-A-0211251 (AUSIMONT S.P.A.) * claims * * example *	1-4	/(C08F214/22, 216:14) (C08F214/26,21 6:14)
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 OCTOBER 1990	Examiner HOFFMANN K.W.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			